

Structural And Conductivity Studies Of $\text{Li}_4\text{Ti}_5\text{O}_{12}$

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Abstract

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ has been successfully synthesized via the sol-gel method. The powders were calcined at 700 °C, 800 °C, 900 °C and 1000 °C for one hour followed by pellet formation at 500 bars and sintering at 1000 °C for four hours. Electrochemical impedance spectroscopy (EIS) and X-Ray Diffraction (XRD) were employed to characterize the prepared $\text{Li}_4\text{Ti}_5\text{O}_{12}$. XRD pattern shows that $\text{Li}_4\text{Ti}_5\text{O}_{12}$ are crystalline and impurities of the prepared sample pellet can be eliminated by double heat treatment. The conductivity obtained is of the order $10^{-8} \text{ S cm}^{-1}$ at room temperature.

Keywords: $\text{Li}_4\text{Ti}_5\text{O}_{12}$, conductivity, XRD pattern

1. INTRODUCTION

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ has attracted much attention as anode material for lithium ion batteries due to its excellent cycling performance [1-4]. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ are zero-strain materials which is defined as materials undergoing small changes in volume expansion during charge and discharge when it is cycled in the voltage range from 0 V to 3.0 V [5-6]. It has charge and discharge plateaus at 1.5 V and a theoretical capacity of 175 mAhg^{-1} [7-8].

Huang and co-workers [9] have synthesized $\text{Li}_{3.92}\text{Ti}_5\text{O}_{11.96}$ via the solid state reaction which has a conductivity of $3.7 \times 10^{-9} \text{ S cm}^{-1}$ at ambient temperature. Previous works have reported that the conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ increased after with Mg^{2+} doping on the Li^+ sites [10] and the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ lattice parameter dopants with Ga^{3+} , Co^{3+} and Al^{3+} tend to decrease since the ionic radii such as Ga^{3+} , Co^{3+} , Al^{3+} are smaller than Ti^{4+} and Li^+ [9]. Other techniques to enhance conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is by forming composites with a conductive second phase [11]. Wolfenstine and Allen [12] have doped Ta elements in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ in order to substitute

Ta^{5+} ion on a Ti^{4+} sites and the conductivity obtained is $3 \times 10^{-8} \text{ S cm}^{-1}$.

Generally, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powders were mainly synthesized by solid-state reactions [13-14] and sol-gel methods [15-16]. To synthesize the material directly by solid-state method requires high calcination temperatures which results in inhomogeneity and contamination of the final products [17-18]. In the sol-gel method, inhomogeneity is overcome during mixing at the atomic or molecular level, synthesis temperature is low, heating time is shorter, and the crystalline particles are distributed uniformly [19-20]. During the sol-gel preparation process, isopropyl alcohol was used to decelerate the sol-gel reaction and avoid the emergence of precipitations [21].

In the present work, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was prepared via the sol-gel technique and characterized using X-Ray Diffraction (XRD) and electrochemical impedance spectroscopy (EIS).

2. EXPERIMENTAL

2.1. Sample Preparation

The prepared powder was synthesized by sol-gel method. Lithium tert-butoxide (LTB) and titanium isopropoxide (TIP) were purchased from Aldrich. 0.05 mol LTB was dissolved in ethanol before mixing with 0.03 mol of TIP. Then, the mixture of water and ethanol was added dropwise to the solution that has LTB and TIP compound. The mixture was then stored for one week followed by filtration. The white powder was calcined at 700 °C, 800 °C, 900 °C and 1000 °C for one hour. 0.5 g of calcined powder was ground using mortar and pestle before pelletization at 500 bars. The pellets were sintered at 1000 °C for four hours and then stored in a dessicator for characterization.

2.2. Sample Characterizations

The prepared sample was characterized by X-Ray Diffractogram (XRD) and electrochemical impedance spectroscopy (EIS). The phase purity and crystal structure of the obtained samples were characterized by XRD. The XRD scan analysis was collected over a 2θ range from 5° to 80°. The surface of the pellets were painted with silver paste. Then, the pellets were sandwiched between stainless steel electrodes. The measurements were carried out from 25 °C to 110 °C. The range of frequency is from 50 Hz to 100 MHz. Conductivity (σ) of the pellet was calculated using Equation (1).

$$\sigma = \frac{t}{R_b A} \quad (1)$$

Here t (cm) is the thickness of the prepared pellet, R_b is bulk resistance in ohms that can be obtained directly from the Cole-Cole plot and A is area of pellet-electrode contact.

3. RESULTS AND DISCUSSION

Fig. 1 shows the XRD pattern of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ calcined at different temperatures (700 °C,

800 °C, 900 °C and 1000 °C for one hour) followed by heat-treatment at 1000 °C for four hours. The prepared samples are crystalline. A peak at $2\theta \sim 20^\circ$ corresponding to Li_2TiO_3 [22-23] was observed in the diffractogram for sample calcined at 700 °C and 800 °C. This peak was successfully eliminated when the samples were calcined at 900 °C and 1000 °C. Hence using the above heat-treatment, a pure compound as reported by Kim and co-workers [24] can be obtained. The other peaks are due to $\text{Li}_4\text{Ti}_5\text{O}_{12}$ compound [25-27].

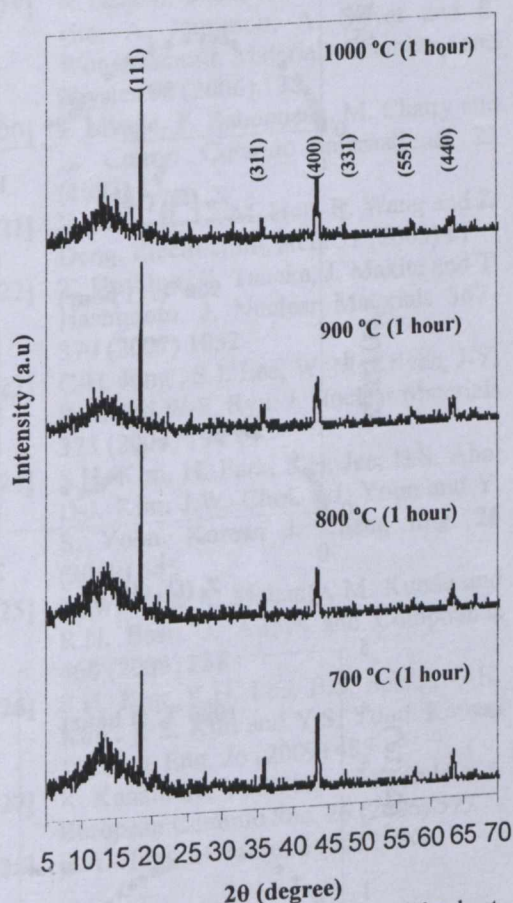


Fig. 1 XRD pattern of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ calcined at different temperatures before sintered at 1000 °C for four hours

Fig. 2 shows the complex impedance plots at ambient temperature of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ which were calcined at different temperatures ranging from 700 °C to 1000 °C. The Cole-Cole plots exhibit semicircle shape which maybe due to mixed ionic and electronic conduction [28].

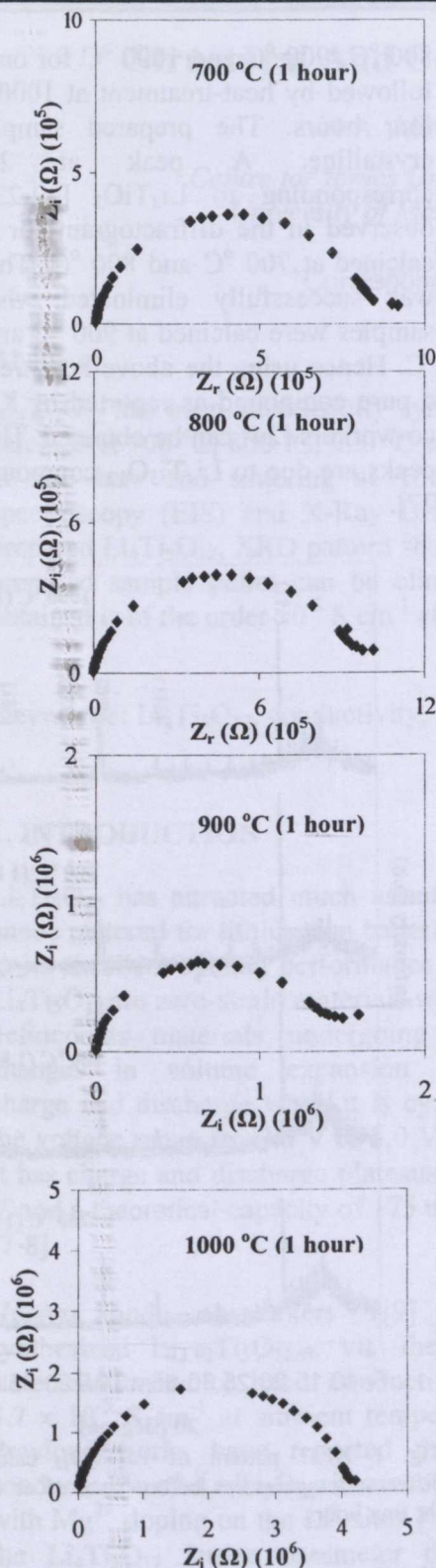


Fig. 2 Complex impedance plot at room temperature of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ calcined at various temperatures

Shown in Fig. 3 is the plot of conductivity versus calcined temperatures. The conductivity of the samples does not differ

significantly although samples calcined at 700 °C and 800 °C for one hour and sintered at 1000 °C four hours contained impurities that can be identified as Li_2TiO_3 [22-23]. The conductivity value of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ obtained in this work is greater than that in previous literature for similar condition [9-12].

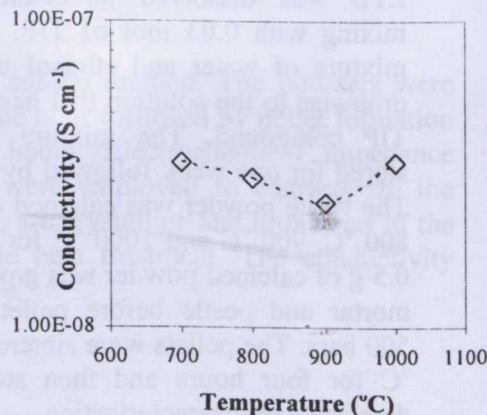


Fig. 3 Plot conductivity versus calcination temperature for one hour at room temperature

Fig. 4 displays the plot of conductivity versus $1000/T$ (K^{-1}) of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ for different heat-treatments. It was found that the conductivity is increased as temperature increased.

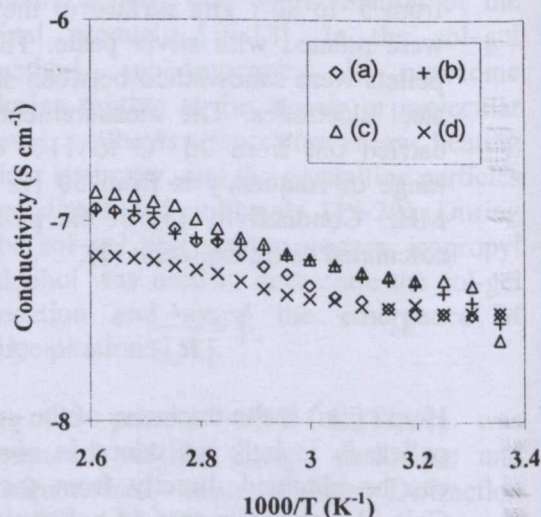


Fig. 4 Plot of $1000/T$ (K^{-1}) versus conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ calcined at (a) 700 °C, (b) 800 °C, (c) 900 °C and (d) 1000 °C for one hour

4. CONCLUSIONS

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ compound has been obtained via the sol-gel method. XRD profile shows that $\text{Li}_4\text{Ti}_5\text{O}_{12}$ obtained is crystalline and two times heat-treatment may eliminate impurity compounds. The conductivity obtained is of the order $10^{-8} \text{ S cm}^{-1}$.

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